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Possible *p*-wave condensed conductor (or superconductor) for $La_{1-x}Ca_xMnO_3$ films

$La_{1-x}Ca_xMnO_3$ 박막에서 p파 초전도의 가능성

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In the ferromagnetic phase with electrons for La_{1-x}(Ca or Sr)$_x$MnO$_3$, films, a remnant resistivity of the order of $10^{-8}\,\Omega m$ is observed up to 100 K and increases exponentially with temperature up to T_c and above one Tesla as a function of magnetic field strength (a positive magnetoresistivity). The phase below T_c is regarded as a polaronic state with a polaronic tunneling conduction. Possible p-wave condensation (or superconductor) with a parabolic density of states and the phase separation are discussed on the basis of the two-fold degeneracy of e_g orbitals.

1. Introduction

For hole-doped manganese oxides La_{1-x}(Ca or Sr)$_x$MnO$_3$, (LCMO or LSMO), colossal (or giant) magnetoresistances (C (or G) MR)(1-3) have been discovered and the polaron ordering[4] was reported. For the ferromagnetism, the correlation between t_{2g} and e_g electrons has been considered very important for over 40 years.(5,6) However, some researchers have indicated that the coupling between the charge and the spin is not strong enough to describe the CMR correctly.(7,8) A small polaronic conduction[9] above T_c and a large polaronic conduction[10] below T_c have been suggested. The LSMO was observed as a half metal with both metallic and semiconducting electronic structures below T_c by the spin-resolved photoemission.[11] The possibility of phase separation was also suggested.(12-14) Two phases, i.e., one metallic and one semiconducting phase were separated by observing magnetoresistances for LCMO thin films.(14,15) The parabolic density of states for the LSMO has been discussed.[15] A model explaining the CMR suggested that the cause of the CMR is due to a carrier density collapse, on the basis of the polaron theory.[16] To take account of the magnetism, the Hubbard Hamiltonian with on-site Coulomb interaction and the two-fold degeneracy of e_g orbitals was also applied.[17] Therefore, the conduction mechanism and an electronic structure for LCMO and LSMO remain unclear to be clarified.

In this paper, we observe both a remnant resistivity and its magnetic field dependence (a positive MR), by the van der Pauw method, in the ferromagnetic phase. Further, temperature dependences of Hall coefficients are shown and the ferromagnetic p-wave condensation is discussed theoretically.

2. Experiment

Thin films were deposited with the $La_{0.67}Ca_{0.33}MnO_3$ ceramic target on (100)MgO substrates at a substrate temperature of 700℃ in oxygen by laser ablation. The deposited LCMO films showed the semiconducting behavior for resistance before annealing. This may be attributed to the lattice mismatch between a film and the MgO substrate. The deposited LCMO films were annealed at 900℃ in oxygen in a furnace and showed the ferromagnetic behavior. The $La_{0.67}Ca_{0.33}Mn_{1.07}O_3$ (LCMO8/10H) and $La_{0.65}Ca_{0.35}Mn_{1.12}O_3$ (LCMO9/15H) films were annealed for ten and fifteen hours, respectively. Their dimensions were 3×3 mm^2 and 3×4 mm^2, respectively, and the thicknesses were 4080Å and 2250Å, respectively. Their LCMO contents were analyzed using the electron probe microanalysis. Ca elements were found to be distributed homogeneously in the films. The films were found to be oriented along the c-axis by an X-ray diffractometer. After annealing films for longer than 4 hours the full width of the half-maximum for X-ray diffraction peaks decreased. The oxygen content and crystalline order might be optimized gradually with annealing time.

Magnetoresistances were measured by the van der Pauw method.(14,15) Hall coefficients were measured along the diagonal direction. The magnetic field was applied to the c-axis of the films in a SQUID of Quantum Design Co.. A nanovoltmeter of Hewlett Packard Co. was used.

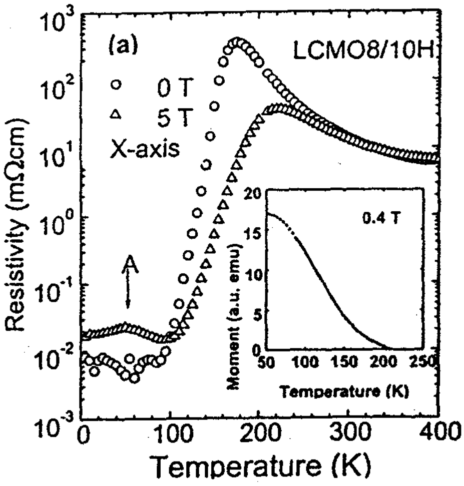

Fig. 1 Temperature and magnetic field dependencies of magnetoresistivities for the LCMO8/10H film. The inset shows the temperature dependence of the magnetic moment.

3. Results and Discussion

Figure 1 shows resistivities measured by the van der Pauw method with $50\,\mu A$ at 0 and 5 Tesla for the LCMO8/10H film. Below 100 K, the remnant resistance voltage and resistivity are measured at 0 Tesla and found to be, on average, $3\,\mu V$ and 10^{-3} $m\Omega cm$ (or $10^{-8}\Omega m$), respectively. The resistivity below 100 K can be regarded as constant with temperature, although there is low-level noise. The resistivity is the same order as that of a $Y_{0.7}Sr_{0.3}MnO_3$ thin film.[18] The resistivity below 100 K increases slightly at 5 Tesla, as indicated by the arrow A in the figure, which may be called a positive MR. The logarithmic resistivities are linear from 100 K to T_c, which indicates nearest neighbour hopping of polarons, as suggested by Hundley et al.[19]. For the resistivity measured at 0 Tesla, in assuming $\rho = \exp(-E/k_BT)$, which is different from the hopping term for a semiconductor, E is estimated to be 157 meV below T_c. This indicates that charges below the Fermi energy contribute to conduction, and that the state below T_c is suggestive of a condensed state. A Hall voltage of a HTCMR for LCMO9/15H is shown in Fig. 2. The Hall voltage were measured at 5 Tesla with 50μA. The negative Hall voltage indicates that carriers are electrons. They can be regarded as electrons in $3d$ band. Below 75 K in inset of Fig. 2, with decreasing temperature, the decreases of the Hall voltage corresponds to the increase of carriers. This indicates a carrier-density collapse, as suggested by Alexandrov and Bratkovsky.[16]

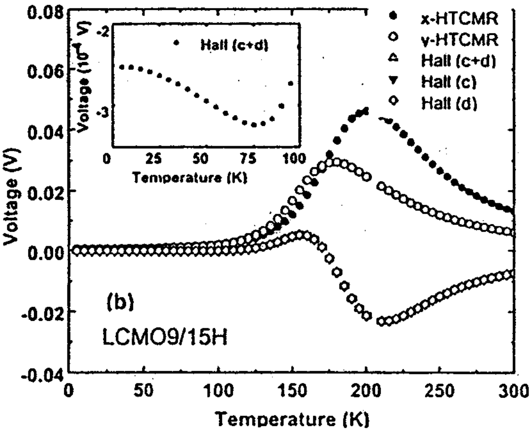

Fig. 2 Temperature dependence of Hall voltages, Hall (c) (a diagonal direction), Hall (d) (another diagonal direction) and Hall (c+d) (average of c+d) for the LCMO9/15H film. The inset is the magnification of the Hall voltage Hall (c+d).

4. Possible p-wave condensation

To find the possibility for condensation of the ferromagnetic phase with electrons, electronic specific heat anomalies were observed for a ceramic $La_{0.67}Ca_{0.33}MnO_3$ by Ramirez et al.[20] and $La_{0.8}Ca_{0.2}MnO_3$ by Tanaka and Mitsuhashi[21]. Tanaka and Mitsuhashi suggested the heat anomaly as evidence of a second-order transition. The shape of the anomalies is asymmetric in spite of symmetry for a Heisenberg ferromagnet[22] and is similar to that for a superconductor, as shown in Fig. 3. The anomalies may be attributed to condensation rather than to a magnetic interaction.

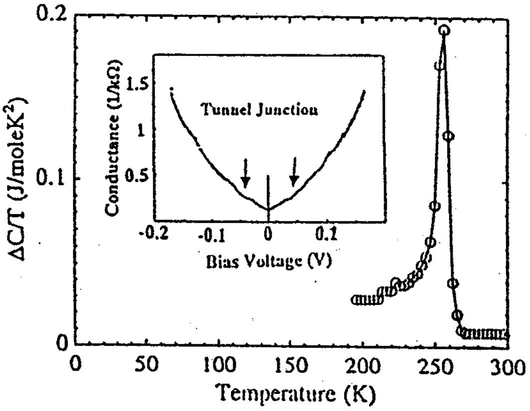

Fig. 3 (a) An electronic specific heat anomaly without a lattice contribution for a ceramic $La_{0.67}Ca_{0.33}MnO_3$, presented by Ramirez et al.[20] The conductance of a tunnel junction for a (b) $La_{0.67}Sr_{0.33}MnO_3$ film, measured at 4.2 K by Yu Lu et al.[23] is shown in the inset.

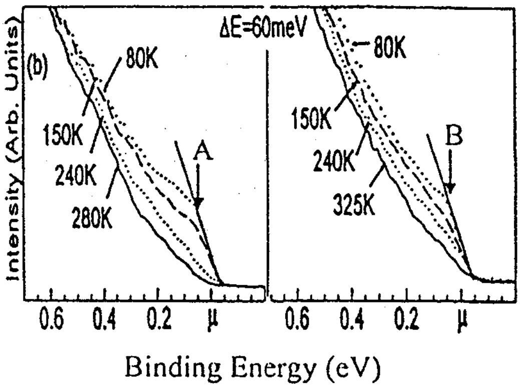

Fig. 4 Temperature dependent PES spectra of (a) $La_{0.67}Ca_{0.33}MnO_3$ and (b) $La_{0.67}Pb_{0.33}MnO_3$ measured by Park et al.[25]. The $h\nu$=110 eV high resolution spectra for near E_F region.

A density of states (DOS) of the ferromagnetic phase, as the conductance of a tunnel junction for Fig. 3, was measured at 4.2 K by Lu et al.[23]. Besides their analysis, we find that the V shape below +-0.05 V in Fig. 3 is attributed to the tunneling of impurity (or holes) carriers, which is suggested by Bratkovsky's model[24].

In addition, spectra intensities, observed by high resolution photoemission spectroscopy (PES) by Park et al.[25], increase rapidly with increasing binding energy by around 0.05 eV indicated by arrows A and B below the Fermi energy at 80 K and 150 K, as shown in Fig. 4. These rapid increases correspond to one side of the *V* shape measured by the tunnel junction mentioned above. The intensities near the Fermi energy are different from those of normal metals. Here, our analysis thus offers an alternative explanation to interesting experimental findings.[25] Except for the *V* shape measured by the tunnel junction and the rapid increase observed by the PES, the DOS is parabolic. The DOS of a ferromagnet[24], a half metal[24], and a p-wave superconductor as the ABM state(26,27) all are parabolic. Therefore the DOS is consistent with *p*-wave (or non s-wave) condensation.

Coey, Viret and Ranno[18] measured heat capacity in the range from 1.5 to 20 K for five samples (LCMO, LSMO, YSMO, NdBaMO, NdSrMO) with x=0.3. They concluded that all samples show the $C = \gamma T + \beta T^3$ variation normally expected of a metal. In view of many experimental behaviors, the ferromagnetic phase does not lead to the simple normal metal. Hence the T^3, also calculated in the *p*-wave conductor,[27] might arise from the p-wave condensation.

Furthermore, a structure-phase transition with the magnetic transition, caused by a large breathing-mode distortion, was observed.[8] The low resistivity, the positive CMR, the nonmetallic temperature dependence of the resistivity below T_c, the second-order transition, and the parabolic DOS indicate that the ferromagnetic conduction is governed not by itinerant carriers but instead by mobile polarons condensed by an attractive potential energy due to a strong electron-lattice interaction which is regarded as the Jahn-Teller effect[7]. We can perhaps call the ferromagnetic phase a ferromagnetic (or *p*-wave) condensed conductor with a polaronic state.

On the basis of the above experimental results, the following model can be considered. The t_{2g} electrons in d bands are strongly localized and e_g electrons are regarded as small polarons in the paramagnetic state (above T_c) and tunneling-polarons in the ferromagnetic state (below T_c). In this case, this system can be regarded as having, above T_c, one e_g electron located at each site, and, below T_c, two e_g electrons located on a site at $d_{(x2-y2)}$ and $d_{(3z2-r2)}$ orbitals (two-fold degeneracy of e_g orbitals) and nearest neighbour sites are empty. Then two e_g electrons are bound by the electron-ion interaction due to the Jahn-Teller distortion. The ferromagnetism arises from the Hund coupling (J is positive) of two electrons on site. Two electrons form a triplet bipolaron with total spin-one. The dynamics of this system may be modeled by a Hubbard Hamiltonian including the effective potential

$$V'(T)=-V+U+J(T), \qquad \text{---------------} \ (1)$$

where $V=4E_p$ is Holstein's electron-lattice interaction[28] with a short range due to the Jahn-Teller distortion (V represents the small bipolaron binding energy); E_p is the polaron binding energy, U is the on-site Coulomb (Hubbard) interaction, and J is Hund's exchange coupling and is positive. $J(T)$ starts to be generated with decreasing temperature from T_c and nearest neighbour hopping with bipolaron-polaron pair-breaking begins to occur with increasing temperature from T_c. Above T_c, U and J become zero, and $V = E_p$. Below T_c, with increasing $U+J$, V' decreases. In a large $U+J$ case, $|V'|$ can become smaller than E_p. Then the triplet bipolaron with S=1 can tunnel through the attractive potential barrier.

Therefore, current flows below T_c. This model is different from the double exchange model[4] and is similar to a model[17] with the two-fold degeneracy of e_g orbitals. Furthermore, the potential V depends upon doping concentrations and has an instability at the transition point of the metal-insulator transition (MIT).[29] Because of the instability, the exact MIT can not occur. For this reason, in Mn systems, the ferromagnetic phase and the antiferromagnetic insulating phase coexist. Therefore the cause of the phase separation is due to the metal-insulator instability[29].

If J=0 and the spin directions of two electrons are opposite, the pair becomes a singlet bipolaron with the diamagnetic characteristic. The triplet (S=1) or the singlet (S=0) bipolarons are the mobile carriers below the Fermi energy. The conductors with S=1 and S=0 are p-wave and s-wave, respectively. For this reason, Mn systems can be interpreted as p-wave condensed conductors (or superconductors). The reason why the p-wave conductor had not been discovered is that the ferromagnetic transport characteristic of a very low resistivity was screened by the semiconducting characteristic arising from an extrinsic effect.

5. Conclusion

In conclusion, we found the ferromagnetic polaronic condensed phase having an exponential temperature dependence of the resistivity of the order of $10^{-8}\Omega m$ which increases above 1 Tesla. The density of states of the ferromagnetic phase is p-wave like. Further, on the basis of two-fold degeneracy of e_g orbitals for Mn systems, the p-wave condensation can occur.

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